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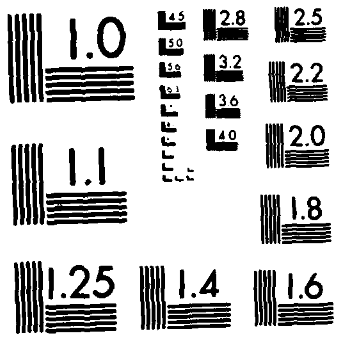

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SYNTHESIS OF IONIC CONDUCTING INTERPENETRATING POLYMER NETWORKS

by

C. K. Chiang, B. J. Bauer, R. M. Briber and G. T. Davis,

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Synthesis of Ionic Conducting Interpenetrating Polymer Networks

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ABSTRACT

Epoxy and ionic conducting poly(ethylene oxide)-salt complexes form interpenetrating polymer networks. The co-continuity of the two phases are tested independently using mechanical and electrical measurements. Examination of the network using transmission electron microscopy suggests that the size scale of the phases ranges from 0.1 to 0.5 microns.

*Partially supported by the Office of Naval Research.

INTRODUCTION

The discovery of high ionic conductivity in poly(ethylene oxide)-salt complexes[1,2] has led to an extensive search for solid polymeric electrolytes.[3-5]

The desirable properties for a solid polymeric electrolyte include both high ionic conductivity and good mechanical strength. Attempts to increase ionic conductivity by lowering the molecular weight or the glass transition temperature result in specimens that are fluids or mechanically weak films. Crosslinking can lead to stronger films, but generally results in a drop in conductivity. The largest research effort previously has been on single phase polymers with capability to dissolve salts and to form polymer-salt complexes.[6-8] However, the conductivity of these polymer systems is only on the order of 1 X 10^{-6} S/cm at room temperature.

To find a polymer system which has both high ionic conductivity and good mechanical properties, we have focused our attention on interpenetrating polymer networks, IPNs.[9,10] This paper reports the first attempt to synthesize an ionic conducting IPN made from epoxy and poly(ethylene oxide)-salt complexes. The epoxy forms the phase which has good mechanical properties while the liquid PEO-salt complex phase provides the high ionic conductivity. In an ideal IPN each co-continuous phase provides one of the necessary properties.

EXPERIMENTAL

Poly(ethylene oxide), MW=400 (Aldrich)[11], and 10 mole %

lithium perchlorate were dissolved in spectro grade acetonitrile to form a 5 wt% solution. The PEO solution was mixed with the epoxy, diglycidylether of bisphenol A (Dow DER-332) [11] and crosslinker, poly(propylene oxide) triamine (Texaco Jeffamine T-403). [11] Acetonitrile was evaporated at room temperature in vacuum. The dried mixture was cured at 95 °C.

The electrical conductivity of the polymers was measured using the AC impedance method. The electrodes were a pair of stainless steel plates pressed against the surface of the polymer films (15mm x 15 mm). The specific conductivity of the sample was deduced by varying the AC frequency from 100 Hz to 13 MHz. The frequency data was also used to examine the relaxation mechanism of the polymer. Compression modulus was measured by placing a series of dead weights on the sample. The displacement of sample was measured 30 seconds after each weight was applied. The modulus of the polymer was computed by a linear least squares fitting of the force versus displacement.

RESULTS AND DISCUSSION

The pure epoxy is a rigid solid with a conductivity of less than 10^{-12} S/cm at room temperature. The epoxy containing the PEO-salt complex phase is a opaque white solid. For less than 20 wt% epoxy phase, no free standing film was able to be formed, which would indicate that the epoxy did not form a continuous phase. When the epoxy content is more than 20 wt%

free standing films were formed.

The mechanical properties of these films improve as the percentage of epoxy increases. Figure 1 shows the modulus as a function of epoxy content from 20 wt. % to 50 wt. %. At 50 wt. % epoxy the measured modulus is 2.5×10^9 dynes/cm^2. This agrees with the Young's modulus of a pure epoxy, which is 2×10^9 dynes/cm^2.[12] At about 30 wt% of epoxy the modulus of the polymer sample still has a value approaching that of the pure epoxy. The formation of a free standing film with 20 wt. % or more epoxy is evidence that the epoxy phase is continuous.

At room temperature the PEO-$LiClO_4$ complex is a viscous liquid. The dissociated Li^+ and ClO_4^- ions provide ionic conductivity of 6×10^{-4} S/cm. The viscosity of the PEO polymer increases when the salt is incorporated. The viscosity increase is due to the crosslinking effect by the dissolved ions. The AC electrical impedance spectrum of PEO-10 mol% $LiClO_4$ shows a simple RC response with a small depression angle. The DC electrical conductivity is calculated from the minimum in the complex impedance plot. The ionic conduction follows a free-volume mechanism [13-14].

Figure 2 shows the DC electrical conductivity of the polymers as a function of epoxy content from 20 wt. % to 50 wt.%. The conductivity of the polymer remains nearly constant from pure PEO-$LiClO_4$ to about 30 wt% epoxy. Further increase in epoxy content leads to an exponential decrease in the conductivity. The AC electrical impedance spectra of the

polymers with up to 35 wt% of epoxy shows a similar RC response as that of the polymer with no epoxy added. This behavior indicates that the samples containing 35 wt % and less epoxy maintain a continuous conducting phase. Above 40 wt. % of epoxy the impedance spectra of the polymers show evidence of distributed relaxation. This type of spectra is often observed in a polycrystalline ionic conductor which contain grain boundaries.[15] It can be interpreted that at higher epoxy contents the phase separated epoxy is beginning to restrict the motion of ions.

A sample of 50 wt% epoxy and 50 wt% PEO-salt complex has been examined using transmission electron microscopy (TEM). Phase separation was observed on the size scale of 0.1 to 0.5 microns. The corresponding AC impedance spectrum of the polymer with 50 wt. % epoxy is highly depressed. The AC impedance spectrum indicates that the connection of PEO-salt phases are highly non-uniform since the spectrum did not exhibit two clearly separated RC responses. Also, the conductivity of the IPNs never dropped to the level of pure epoxy.

CONCLUSIONS

In conclusion, co-continuous interpenetrating polymer networks are formed between epoxy and PEO-Li salt complexes when the epoxy content varies between 20 wt % to 50 wt % based on electrical and mechanical measurements. The optimum properties for a solid polymeric electrolyte are in the vicinity of 30 wt% epoxy and 70 wt% PEO-$LiClO_4$ in the present

system.

Forming an IPN will have many advantages over a single phase polymer system. Two aspects should be emphasized: first, that all existing ionic conducting polymer systems could be used, even if they are in liquid form, to construct solid IPN electrolytes. Second, a suitable choice of the support phase could provide good thermal and mechanical properties. The concept presented in this paper involves a new process for preparing solid polymeric electrolytes.

In our experiments the concentration of $LiClO_4$ salt was fixed at 10 mole %. Although it was not optimized for the best conductivity, an IPN system with a conductivity of 1×10^{-4} S/cm at room temperature has been obtained. This ionic conductivity is nearly ten times higher than the values reported for systems such as polyphosphazine or polysiloxane containing lithium salts.[6-8]

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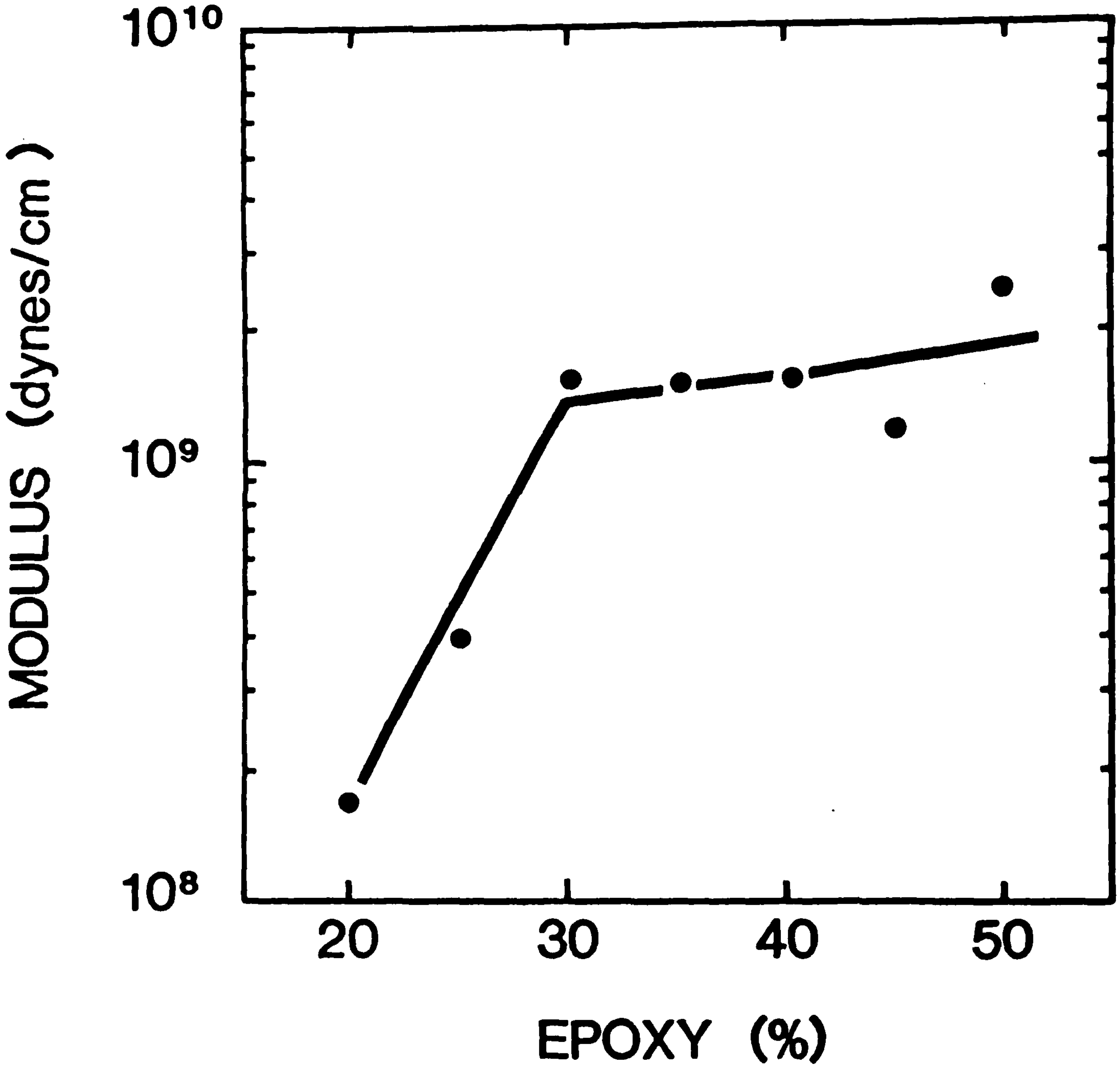
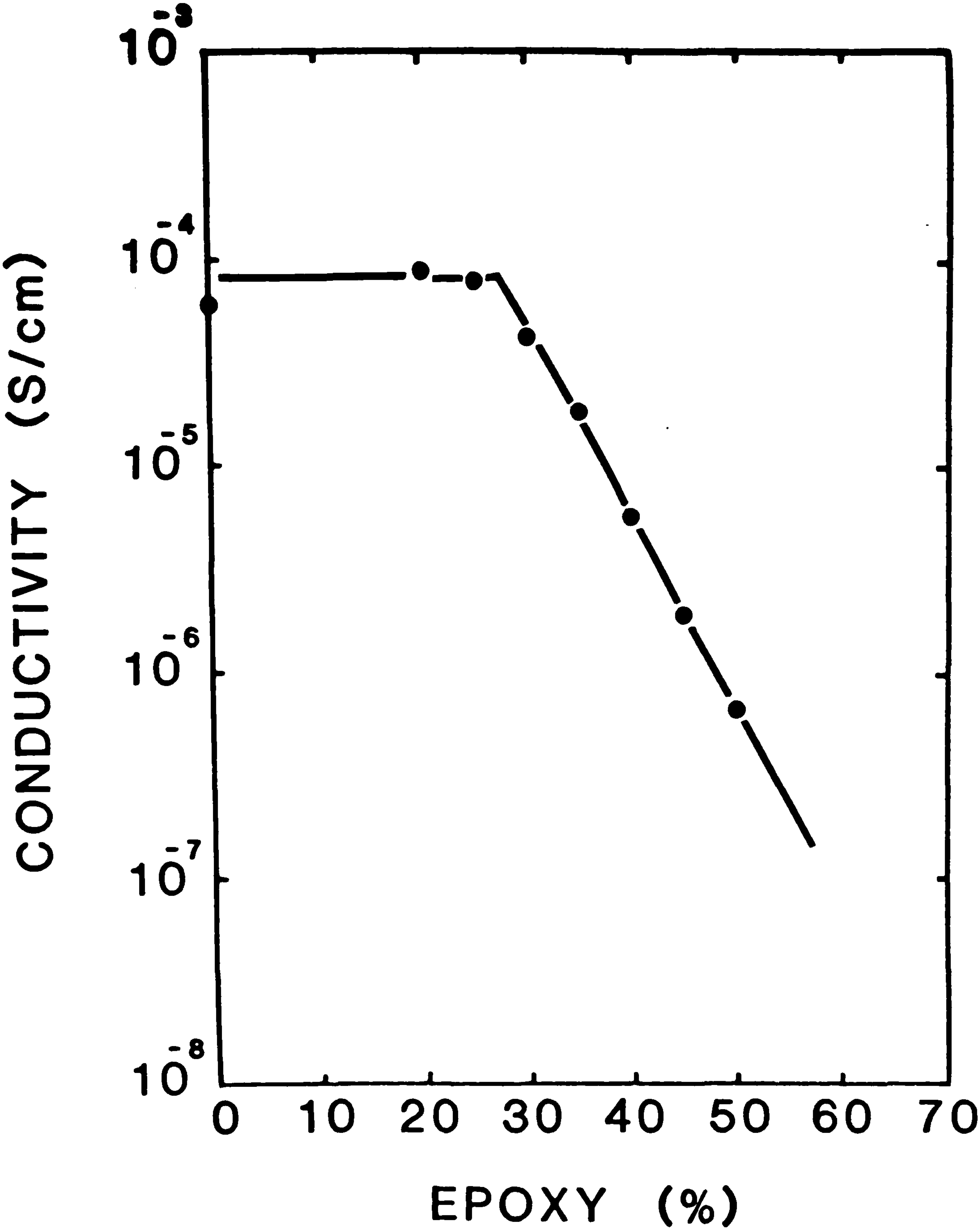
FIGURE CAPTIONS

Figure 1. The Modulus of epoxy/PEO-10 mol.% $LiClO_4$ samples as a function of epoxy content. The straight lines are the least squares fit for data above and below 30 wt%.

Figure 2. The electrical conductivity of epoxy/PEO-10 mol.% $LiClO_4$ samples as function of epoxy content. The straight lines are the least squares fit for the data above and below 30 wt%.


MODULUS (dynes/cm)
10^10
10^9
10^8
20
30
40
50
EPOXY (%)



10^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{-7}
10^{-8}
CONDUCTIVITY (S/cm)
0
10
20
30
40
50
60
70
EPOXY (%)

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